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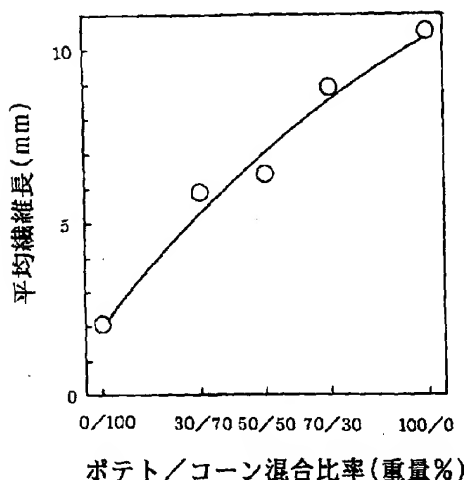
(57) [Abstract]

【課題】複合化させる微細粒子の量に拘らず、維長を任意に制御することができる微細粒子複合化デンプン繊維の製造方法を提供する。

[Problem] Manufacturing method of fine particle composite making starch fiber which can control maintaining length in the option regardless of quantity of fine particle which composite making is done, is offered.

【解決手段】デンプンと微細粒子の混合コロイド分散液を紡糸することによって微細粒子複合化デンプン繊維を製造する方法において、原料微細粒子の混合比率をデンプンと微細粒子の合計重量に対して90重量%以下とし、原料デンプンとして曳糸性のあるデンプンと曳糸性のないデンプンとの混合物を使用し、曳糸性のあるデンプンと曳糸性のないデンプンとの混合比率を変えることにより微細粒子複合化デンプン繊維の平均繊維長を任意に制御することができる。

[Means of Solution] In method which produces fine particle composite making starch fiber by yarn-spinning doing mixed colloid dispersion of starch and fine particle regarding, mixing ratio of starting material fine particle is designated as 90 wt% or less vis-a-vis total weight of starch and fine particle, blend of starch which has fiber pulling behavior as starting material starch and starch which does not have fiber pulling behavior can be used, the mean fiber length of fine particle composite making starch fiber can be controlled in option by changing the mixing ratio of starch which has fiber pulling behavior and starch which does not have fiber pulling behavior.



【特許請求の範囲】

【請求項１】 デンプンと微細粒子の混合コロイド分散液を紡糸することによって微細粒子複合化デンプン繊維を製造する方法において、原料微細粒子の混合比率をデンプンと微細粒子の合計重量に対して９０重量％以下とし、原料デンプンとして曳糸性のあるデンプンと曳糸性のないデンプンとの混合物を使用し、曳糸性のあるデンプンと曳糸性のないデンプンとの混合比率を変えることにより微細粒子複合化デンプン繊維の平均繊維長を制御することを特徴とする微細粒子複合化デンプン繊維の製造方法。

【請求項２】 曳糸性のあるデンプンとして馬鈴薯デンプンを、曳糸性のないデンプンとしてトウモロコシデンプンを使用する請求項１記載の微細粒子複合化デンプン繊維の製造方法。

【請求項３】 原料微細粒子の混合比率をデンプンと微細粒子の合計重量に対して３０重量％以上７０重量％以下とする請求項１記載の微細粒子複合化デンプン繊維の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】 この発明は微細粒子複合化デンプン繊維の製造方法に関し、より詳しくは、用途に応じて複合化する微細粒子の量を選定でき、かつ任意の平均繊維長を有する微細粒子複合化デンプン繊維を得ることができる、新規かつ改良された微細粒子複合化デンプン繊維の製造方法に関するものである。

【０００２】

【従来の技術】 デンプンをパルプ状にしたデンプン繊維は、例えば木材パルプの全部または一部の代替材料として従来から使用されており、木材パルプに混合して抄紙することにより紙の強度特性を改善したり、抄紙時に使用する内添薬品の保持率を向上する等の効果が得られている。またデンプン繊維の透明性を利用してグラシン紙の製造に際して木材パルプと混合使用されている。

[Claim(s)]

[Claim 1] In method which produces fine particle composite making starch fiber by yarn-spinning doing mixed colloid dispersion of starch and fine particle regarding, manufacturing method of fine particle composite making starch fiber which designates that mean fiber length of fine particle composite making starch fiber is controlled by changing mixing ratio of starch where it designates the mixing ratio of starting material fine particle as 90 wt% or less vis-a-vis total weight of starch and the fine particle, uses blend of starch which has fiber pulling behavior as the starting material starch and starch which does not have fiber pulling behavior, has fiber pulling behavior and the starch which does not have fiber pulling behavior as feature.

[Claim 2] As starch which has fiber pulling behavior manufacturing method of fine particle composite making starch fiber which is stated in Claim 1 which uses corn starch potato starch, as starch which does not have fiber pulling behavior.

[Claim 3] Manufacturing method of fine particle composite making starch fiber which is stated in Claim 1 which designates the mixing ratio of starting material fine particle as 30 weight % or more 70 wt% or less vis-a-vis total weight of starch and fine particle.

[Description of the Invention]

[0001]

[Technological Field of Invention] This invention regards manufacturing method of fine particle composite making starch fiber, furthermore details according to application be able to select quantity of the fine particle which composite making is done, can acquire fine particle composite making starch fiber which at same time possesses mean fiber length of option, novel and it is something regarding manufacturing method of fine particle composite making starch fiber which is improved.

[0002]

[Prior Art] Or other effect which improves has been acquired retention of the internal addition chemical where starch fiber which designates starch as pulp is used from until recently as substitute material of all or part of for example wood pulp, mixes to the wood pulp and improves strength characteristic of paper by papermaking doing, uses at time of papermaking. In addition wood pulp and mixed use it is done at time of the production of glassine paper making use of transparency of starch fiber.

【0003】 どのようなデンプン繊維の製造方法としては、デンプンの水懸濁液を加熱あるいはアルカリ処理してデンプンのコロイド分散液とし、これを硫酸アンモニウム等の水溶液からなる凝固浴中に糸条の流れにして押出して凝固させる方法や、デンプン水懸濁液をジェット・クーキング法により煮沸溶解したデンプンコロイド分散液を凝固浴中で凝固させる方法等が種々提案されている（例えば米国特許第4139699号、特公昭60-35480号、特表平7-502312号等）。

【0004】 上述した製造方法で得られるデンプン繊維の繊維長は、例えば特表平7-502312号では1mm未満、特公昭60-35480号では0.1~3.0mmと記載されている。しかしながら、デンプン繊維を例えば製紙分野に利用する場合には、繊維長が極端に短ければ抄紙時にワイヤーから抜けてしまい本来の目的が達成できず、一方、繊維長が長すぎても繊維同士が結束したまま巻き込まれてしまうという不都合が生じる。

【0005】 そこで本発明者らは鋭意検討を行い、目的に応じて任意の繊維長を有するデンプン繊維を製造できる方法を開発して既に特許出願を行った（特願平6-154672号）。この先願発明は、原料デンプンについて支糸性ある種と支糸性のない種とがあり、それぞれ繊維長の長いデンプン繊維および短いデンプン繊維をもたらし、両方の種を適宜割合に混合した原料デンプンを用いることで混合比率に応じ任意の繊維長分布を有するデンプン繊維が得られることを見いだしたものである。このようにして得られる所望の繊維長分布を有するデンプン繊維により、所望の使用目的が効果的に達成でき、さらには今までには考えられなかった効果が生じることも期待できる。

【0006】 また、上述した特公昭60-35480号ではデンプン分散物全体に均等に水不感性添加物、例えば顔料、金属粉末、ラテックス等を混合してデンプン繊維に封じ込めた形態で包含させることを提案している。特表平7-502312号においてもデンプン懸濁液に有機増量剤、鉱物を含有することができるとしている。

[0003] As manufacturing method of this kind of starch fiber, heating or alkali treatment doing the aqueous suspension of starch, method of making colloid dispersion of starch, doing to push out in coagulation bath which consists of ammonium sulfate or other aqueous solution in flow of the yarn clotting doing this starch aqueous suspension method etc which clotting is done various has been proposed starch colloid dispersion which you boil melt with jet * cooking method in coagulation bath, (Such as for example U. S. Patent No. 4139699 number, Japan Examined Patent Publication Sho 60 - 35480 number and Japanese Publication of International Patent Application 7 - 502312 number).

[0004] Fiber length of starch fiber which is acquired with manufacturing method which the description above is done is stated, with for example Japanese Publication of International Patent Application 7 - 502312 number under the 1 mm, with Japan Examined Patent Publication Sho 60 - 35480 number 0.1 to 3.0 mm. But, when starch fiber is utilized in for example papermaking field, if fiber length is short extremely, to come out from wire at time of papermaking and not be able to achieve original objective, while on one hand, fiber length is too long and fiber bundle is done to make paper undesirable that occurs is packed.

[0005] Then these inventors did diligent investigation, developing method which can produce the starch fiber which possesses fiber length of option according to the object, already did patent application, (Japan Patent Application Hei 6 - 154672 number). It is something which discovers fact that starch fiber which possesses fiber length distribution of option according to mixing ratio is acquired by the fact that starting material starch where this Prior Application is with a kind which is the fiber pulling behavior concerning starting material starch and a kind which does not have fiber pulling behavior, the starch fiber where fiber length is long respectively and brings short starch fiber, mixes kind of both to as needed ratio is used. Be able to achieve to effective desired use objective, furthermore to now, you can expect also that effect which was not thought occurs with the starch fiber which possesses desired fiber length distribution which is acquired in this way.

[0006] In addition, with Japan Examined Patent Publication Sho 60 - 35480 number which description above is done the water non-sensitivity additive, mixing for example pigment, metal powder and latex etc to the starch dispersion entirely equally, you propose that it includes with form which you enclose to starch fiber. We have assumed that organic extender and mineral can be contained in the starch suspension, regarding Japanese Publication of International Patent Application 7 - 502312 number.

【0007】

【発明が解決しようとする課題】しかしながら上記したような水不感性添加物をデンプン繊維に包含させた場合においても、問題となるのはデンプン繊維の繊維長であり、例えば顔料のような粉末添加物を使用して何らかの機能性をデンプン繊維に付与しようとする場合でも、用途に応じてデンプン繊維の繊維長を制御できなければ使用目的を効果的に達成できないことになる。また、添加物によってはデンプン繊維内に多量に含有させなければ機能が発現されないものもあり、多量に添加できた場合でもデンプン繊維の繊維長を任意に制御できなければ、付加価値の高いデンプン繊維が得られない場合もある。

【0008】そこでこの発明は、目的に応じて任意の繊維長が得られ、しかも複合する微細粒子の量を広い範囲で選択できる微細粒子複合化デンプン繊維の製造方法を提供することを目的としてなされたものである。

【0009】

【課題を解決するための手段】本発明者はさらに研究を進めた結果、微細粒子を混合した系においても、曳糸性のあるデンプンと曳糸性のないデンプンとを適宜の割合で混合することにより、混合比率に応じ繊維長分布を任意に制御できること、かような特性が微細粒子の混合率が極めて大きい場合においても保たれることを見だし、この発明を完成させたものである。

【0010】すなわちこの発明は、デンプンと微細粒子の混合コロイド分散液を紡糸することによって微細粒子複合化デンプン繊維を製造する方法において、原料微細粒子の混合比率をデンプンと微細粒子の合計重量に対して90重量%以下とし、原料デンプンとして曳糸性のあるデンプンと曳糸性のないデンプンとの混合物を使用し、曳糸性のあるデンプンと曳糸性のないデンプンとの混合比率を変えることにより微細粒子複合化デンプン繊維の平均繊維長を制御することの特徴とする微細粒子複合化デンプン繊維の製造方法である。

【0011】

【発明の実施の形態】この発明において微細粒子とは、顕微鏡で観測可能な小寸法の物体を指す。一般に微細とは、顕微鏡で区別できる程度の細かいものを指し、粒子とはJIS Z 8122によれば、観測可能な長さ、幅及び厚さを持つ小寸

【0007】

[Problems to be Solved by the Invention] But, when water non-kind of sensitivity additive which was inscribed is included in starch fiber in, Using powder additive where fact that it becomes problem is fiber length of starch fiber, like for example pigment, if, it cannot control fiber length of the starch fiber even with when it tries to grant a some functionality to starch fiber according to application, it means not to be able to achieve use objective to effective. In addition, if inside starch fiber it is not contained in large amount depending upon additive, there are also some where function is not revealed and if even with when it can add to large amount they cannot control fiber length of starch fiber in option, when starch fiber where the added value is high is not acquired, it is.

【0008】 Then quantity of fine particle where as for this invention n, fiber length of option is acquired according to objective, furthermore compounds it is something which can do that manufacturing method of fine particle composite making starch fiber which can be selected in wide range is offered as objective.

【0009】

[Means to Solve the Problems] As for this inventor furthermore of advancing research as for result, Regarding system which mixes fine particle, fiber length distribution can be controlled in option by mixing with starch which has fiber pulling behavior and starch which does not have fiber pulling behavior at appropriate ratio, according to mixing ratio, when this kind of characteristic of blend ratio of fine particle quite is large in, it is something which discovers the fact that it is maintained, completes this invention.

【0010】 Namely as for this invention, In method which produces fine particle composite making starch fiber by yarn-spinning doing mixed colloid dispersion of starch and fine particle regarding, It is a manufacturing method of fine particle composite making starch fiber which designates that mean fiber length of the fine particle composite making starch fiber is controlled by changing mixing ratio of starch where it designates mixing ratio of starting material fine particle as 90 wt% or less vis-a-vis total weight of the starch and fine particle, uses blend of starch which has the fiber pulling behavior as starting material starch and starch which does not have fiber pulling behavior, has the fiber pulling behavior and starch which does not have fiber pulling behavior as feature.

【0011】

[Embodiment of Invention] Fine particle, it points to physical a rticle of observation possible small dimension with microscope at time of this inventing. Generally fine, it points to those where extent which can be distinguished with microscope is

法の物体、と定義されている。例えば、固体粒子の場合はその製法により大きく二つに分けられ、天然物もしくは合成物について大きな塊を粉碎して得たものと化学反応によって得たものである。より細かくは固体を粉碎して得たもの、酸化、還元、熱分解等の化学反応によって得たもの、液体から沈澱もしくは電気析出させて得たもの、溶融状態から粉霧固化して得たもの、気体から凝縮して得たもの、化学物蒸気の熱分解により得たものに分けられるが、その製法を問わずいずれもこの発明における微粒子として好適に使用することができる。

【0012】本発明で使用できる具体的な微細粒子としては、アルミニウム、珪素、チタン、クロム、鉄、コバルト、ニッケル、銅、亜鉛、銀、錫、タングステン、白金、金等の金属粉；カオリナイト、ハロサイト、セリサイト、ゼオライト、ケイソウ土等の粘土鉱物粉体；酸化マグネシウム、アセチレンブラック、バリウムフェライト、黒鉛、磁性トナー等の電気・磁気粉体；ホワイトカーボン、酸化チタン、亜鉛華、炭酸カルシウム、微粒子無水シリカ、銅フタロシアニンブルー、硫化亜鉛カドミウム蛍光体等の有機・無機充填剤粉体；アクリル、ポリエチレン、ナイロン、MBS樹脂、プラスチックピグメント、マイクロカプセル等の有機ポリマー系粉体；マイクロファイブリル化セルロース、結晶セルロース等の微細繊維状物；コーヒー、緑茶、紅茶等を抽出した残滓を微細化した粉体；ラテックスやエマルジョン等を挙げることができる。また、必要によっては2種類以上の組み合わせで微粒子混合物として使用することもできる。

【0013】微細粒子の量や粒度、組み合わせ等は、用途に応じて好ましい条件をあらかじめ予備実験で求めておくことが好ましい。微細粒子については、製造する微細粒子複合化デンブ繊維の大きさによって決められるが、紡糸工程で使用するノズル径よりは小さい直径としなければならない、一般的には直径100μm以下、好ましくは50μm以下がよい。特に直径1μm以下の粒子に関しては、その表面活性エネルギーによって二次凝集を起こし易いため、必要に応じてカチオン性界面活性剤、アニオン性界面活性剤、ノニオン性界面活性剤もしくは両性界面活性剤等を適量添加することにより二次凝集を防止できる。

【0014】この発明において、曳糸性のないデンブとは

small, particle according to the JIS Z8122, observation possible length, physical article of small dimension which has width and thickness, with it is defined. In case of for example solid particle it is something which it acquires with thing and chemical reaction which are divided by two broadly by production method, the powder fragment doing big lump concerning natural product, or synthetic substance they acquire. Those which are smaller and powder fragment doing solid, they acquire. Those which are acquired with oxidation, reduction and the thermal decomposition or other chemical reaction. Precipitation or electricity precipitating from liquid, those which it acquires. powder mist solidification doing from molten state, those which it acquires. condensation doing from gas, those which it acquires. It is divided into those which are acquired with thermal decomposition of the compound vapor you can use for ideal as microparticle in each case in this inventing, but regardless of production method.

[0012] aluminum, silicon, titanium, chromium, iron, cobalt, nickel, copper, zinc, silver, tin, tungsten, platinum, gold or other metal powder; kaolinite (DANA 71.1.1.2), halloysite (DANA 71.1.1.4), sericite, zeolite, diatomaceous earth or other clay mineral powder; magnesium oxide, acetylene black, barium ferrite, graphite, magnetic toner or other electricity * magnetic powder; white carbon, titanium dioxide, zinc white, calcium carbonate, microparticle anhydrous silica, copper phthalocyanine blue, zinc cadmium sulfide phosphor or other organic * inorganic filler powder; acrylic, polyethylene, nylon, MBS resin, plastic pigment, microcapsule or other organic polymer powder; microfibrillated cellulose, crystalline cellulose or other fine fiberones; powder which remnants which extracts coffee, green tea, black tea etc narrowing is done; latex and emulsion etc can be listed as exemplary fine particle which can be used with this invention. In addition, 2 kinds or more combining depending upon necessary, it can also use as microparticle blend.

[0013] As for quantity and granularity and combination etc of fine particle, it is desirable to seek desirable condition beforehand with preparatory experiment according to application. Concerning fine particle, it is decided by size of fine particle composite making starch fiber which is produced, but if it does not make diameter where is smaller than the nozzle diameter which is used with yarn-spinning step it does not become, diameter 100 μm or less and the preferably 50 μm or less are good generally. Especially, because secondary cohesion is easy to happen in regard to the particle of diameter 1 μm or less, with surface activity energy, secondary cohesion can be prevented by the according to need cationic surfactant, anionic surfactant, nonionic surfactant or amphoteric surfactant etc suitable amount adding.

[0014] At time of this inventing, starch which does not have the

、下記の方法によりデンプン繊維を調製した場合に、平均繊維長分布が約1mm以下のデンプン繊維が得られるものをいい、糸系性のあるデンプンとは、平均繊維長分布が約15mm以上のデンプン繊維が得られるものをいう。

【0015】糸系性の有無を調べるためのデンプン繊維の調製方法は、まずデンプンの10重量%水懸濁液を調製し、これを95℃に加熱・膨潤させてデンプンのコロイド分散液とする。この分散液を55℃の一定温度として、凝固浴中に設置した口径0.4mmのノズルから吐出圧力3kg/cm²で凝固浴中に吐出させる。凝固浴中の凝固液には硫酸アンモニウムの40重量%水溶液を使用し、凝固浴を攪拌してデンプン分散液の吐出方向と凝固液の流れ方向が約45°の角度になるようにする。|

【0016】デンプン繊維の平均繊維長分布の測定は以下の方法により行った。上記のようにして調製したデンプン繊維を凝固浴から取り出してプレパラート上に広げ、乾燥固化した後、投影機で拡大してマップメーターを用いて各繊維の長さを測定する。プレパラート1枚当たり200本程度のデンプン繊維が固化され、1回の試験で10枚のプレパラートを調製し、1種類のデンプンについて3回の試験を行った結果から平均繊維長分布を計算により求める。

【0017】上記の方法によりデンプンからデンプン繊維を実際に調製してみて、糸系性のあるデンプン種と糸系性のない種とを区別することができる。本発明者が行った結果から判明したデンプン種を例示すると次のようになる。|

【0018】糸系性のあるデンプン種：ジャガイモ、キャッサバ（タピオカ）、サトイモ、サツマイモ、ナガイモ、ダイジョ、ヤウテア、ハリイモ、ヤマノイモ、ギネアヤム、インドクワズイモ、キルトスベルマ等。

【0019】糸系性のないデンプン種：トウモロコシ、コムギ、イネ（コメ）、オオムギ、ライムギ、エンバク、モロコシ、アワ、ヒエ、キビ等。

【0020】一般には、植物の茎や根から得られるデンプンは糸系性のあるもの、穀物から得られるデンプンは糸系性の

e fiber pulling behavior, when starch fiber is manufactured with below-mentioned method, mean fiber length distribution has influence where starch fiber of approximately 1 mm or less is acquired, starch which has fiber pulling behavior mean fiber length distribution means that starch fiber of approximately 15 mm or greater is acquired.

[0015] Preparation method of starch fiber in order to inspect presence or absence of fiber pulling behavior manufactures 10 weight % water suspension liquid of starch first, heating* swelling does this in 95 °C and makes colloid dispersion of starch. With this dispersion as constant temperature of 55 °C, from nozzle of aperture 0.4 mm which is installed in coagulation bath with extrusion force 3 kg/cm² it discharges in the coagulation bath. You use 40 weight % aqueous solution of ammonium sulfate to coagulation liquid in coagulation bath, agitate the coagulation bath and discharge direction of starch dispersion and flow direction of coagulation liquid that try it becomes angle of approximately 45 degree.

[0016] It measured mean fiber length distribution of starch fiber with method below. Removing starch fiber which it manufactures as description above from the coagulation bath, it expands on preparation, drying and solidification after doing, it expands with the projector and it measures length of each fiber making use of the map meter. starch fiber of preparation per each 200 extent is done, solidification manufactures preparation of the 10-layer with test of one time, seeks mean fiber length distribution from the result of testing thrice concerning starch of 1 kind with calculation.

[0017] Trying manufacturing starch fiber actually from starch with the above-mentioned method, you can distinguish with starch kind which has fiber pulling behavior and kind which does not have fiber pulling behavior. When starch kind which is ascertained from result this invention doing is illustrated it becomes following way.

[0018] Starch kind: potato which has fiber pulling behavior, cassava (tapioca), Colocasia esculenta Schott, the Ipomoea batatas Lam. (Sweet potato), Dioscorea spp. (Chinese yam) and die di, Yau tear, Eleocharis pellucida Presl, the Dioscorea japonica Thunb. and Ginea yam, India Morus bombycis Koidz potato and kill j bell etc.

[0019] Starch kind: Zea mays L. (Corn) which does not have fiber pulling behavior, wheat, the rice (rice), barley, Secale cereale, oats, sorghum, Setaria italica Beauv. (millet), the Echinochloa frumentacea Link (millet) and Panicum miliaceum L. (millet) etc.

[0020] Generally, as for starch which is acquired from stem and the root of plant those which have fiber pulling behavior. As

ないものという傾向がみられたが、実際にはデンプン繊維を調製して判断する必要がある。また上記で例示したデンプンはいずれも天然デンプンであるが、この発明において使用できるデンプンは天然のものに限らず、加工デンプン等の変性デンプンであっても上記のような糸糸性の有無を確認すれば使用することができる。

【0021】この発明を実施するに際しては、先ず1種類以上の微細粒子と糸糸性のあるデンプンと糸糸性のないデンプンとを任意の比率で混合して微細粒子とデンプン粒子の混合水懸濁液を調製し、これを加熱してデンプンを膨潤させることにより、微細粒子とデンプンの混合コロイド分散液とする。微粒子／デンプン混合水懸濁液中のデンプン濃度が低いと紡糸時に凝集力が低下し、デンプン濃度が高いとデンプン膨潤後の微粒子／デンプン混合コロイド分散液の流動性がなくなり紡糸できなくなる。実験の結果、微細粒子が混ざることによってコロイド分散液の流動性が変わることが判っており、一般には微細粒子を混ぜない場合よりも流動性が良くなりデンプン濃度を高くすることが可能である。しかし、微細粒子の種類、特に平均粒子径が1 μ m以下のものについては逆に流動性を妨げるものがあり、場合によっては分散剤を併用して良好な流動性とする必要となる。微粒子／デンプン混合水懸濁液中の固形分〔デンプン＋微細粒子〕の濃度は、微細粒子およびデンプンの種類によって異なるため一概には決められないが、実験結果から考えると一般的には5～20重量%の範囲の固形分濃度とすることが好ましい。微細粒子の混合比率が大きい場合は微粒子／デンプン混合水懸濁液中の固形分濃度は高くなり、微細粒子の混合比率が小さい場合は微粒子／デンプン混合水懸濁液中の固形分濃度は低くなる。混合水懸濁液の加熱の時間および加熱温度は、デンプンを十分に膨潤させて糊化させ得る時間と温度であればよく、100℃以下の温度でもよい。

【0022】微細粒子の混合比率について述べるならば、デンプンと微細粒子の合計重量に対して微細粒子を90重量%以下とする。90重量%を超えて微細粒子を混合すると、得られた微粒子複合化デンプン繊維は良好な繊維状とならない。一方、微細粒子の混合比率の下限は、微細粒子の種類により一定とならない。すなわち、1重量%程度の混合では微細粒子の混合効果が発現しないものもあれば、0.1重量%程

for starch which is acquired from grain you could see the tendency, thing which does not have fiber pulling behavior, but manufacturing the starch fiber actually, it is necessary to judge. In addition if starch which can be used as for starch which was illustrated at description above in each case is a natural starch but, at the time of this inventing processed starch or other modified starch being not just natural ones, as description above verifies presence or absence of fiber pulling behavior, you can use.

[0021] When this invention is executed, first mixing with fine particle of the 1 kind or more which has fiber pulling behavior and starch and starch which does not have fiber pulling behavior with ratio of option, it manufactures mixed aqueous suspension of fine particle and starch powder, heats this and it makes mixed colloid dispersion of fine particle and starch by swelling doing starch. When starch concentration in fine particle / starch mixed aqueous suspension is low, flocculation power decreases at the time of yarn-spinning, when starch concentration is high, fluidity of fine particle / starch mixed colloid dispersion after starch swelling is gone and yarn-spinning becomes impossible. It understands, that fluidity of colloid dispersion changes result of experiment, due to fact that fine particle blends it is possible the fluidity to become good generally in comparison with when fine particle is not mixed and to make starch concentration high. But, types of fine particle, especially average particle diameter there are some which obstruct fluidity conversely concerning those of 1 μ m or less, jointly using dispersant depending upon in case, also it becomes necessary to make satisfactory fluidity. concentration of solid component [starch + fine particle] in fine particle / starch mixed aqueous suspension is not decided because it differs depending upon types of fine particle and starch unconditionally. When you think from experimental result, it is desirable to make solid component concentration of range of 5 to 20 weight % generally. When mixing ratio of fine particle is large, solid component concentration in fine particle / starch mixed aqueous suspension becomes high, when mixing ratio of fine particle is small, solid component concentration in the fine particle / starch mixed aqueous suspension becomes low. If time of heating mixed aqueous suspension and heating temperature, swelling doing the starch in fully, should have been time when conversion to paste it is possible and temperature, even with temperature of 100 °C or below is good.

[0022] You express concerning mixing ratio of fine particle if is, fine particle is designated as 90 wt% or less vis-a-vis total weight of starch and the fine particle. Exceeding 90 weight%, when it mixes fine particle, fine particle composite making starch fiber which is acquired does not become satisfactory fiber. On one hand, lower limit of mixing ratio of fine particle does not become fixed depending upon types of fine particle. If with

度の微量を混合しても混合効果が発現する微細粒子もある。要するに微細粒子の混合効果が発現する最小有効量以上を混合すればよい。微細粒子の一般的な混合比率は、デンプンと微細粒子の合計重量に対して微細粒子を30重量%以上、70重量%以下である。

【0023】デンプンを膨潤させて得られた微細粒子／デンプン混合コロイド分散液は一旦冷却した後、所定の温度に維持して紡糸するが、紡糸時の混合コロイド分散液の温度は50～60℃に維持することが好ましい。混合コロイド分散液の温度が変化すると粘性が変化するため安定した微細粒子複合化デンプン繊維が得られず、また若しく温度が低下するとデンプンの老化を引き起こすことが知られている。

【0024】次に、所定の温度に維持した微細粒子／デンプン混合コロイド分散液を、密閉容器に入れて一定圧力をかけ、任意の数、口径および形状をもったノズル口から凝固浴中に吐出させる、いわゆる湿式紡糸法により微細粒子複合化デンプン繊維にすることができる。かような湿式紡糸法はビスコース繊維等の紡糸法として従来から慣用されている方法であり、従って既存の紡糸装置を利用することができる。微細粒子複合化デンプン繊維の直径（太さ）は、ノズルの口径を変化させることで調節できる。

【0025】凝固浴中の凝固液としては硫酸アンモニウム、硫酸ナトリウム、硫酸マグネシウム、リン酸アンモニウム、炭酸ナトリウム、塩化アンモニウム等の水中で電解質を生じる塩の水溶液が使用でき、硫酸アンモニウムが特に好ましい。凝固液の濃度が低いと凝集効果が十分に得られず、一般的には30～40重量%濃度の塩水溶液が好ましい。

【0026】凝固浴中の凝固液には常時攪拌を施して凝固液の流れを生じさせておく。凝固液の流れの方向と速度は、得られる微細粒子複合化デンプン繊維の繊維長や強度に影響を及ぼす。すなわち、凝固液中に吐出された微細粒子／デンプン混合コロイド分散液が安定した糸条の流れとなるようにするには、混合コロイド分散液の吐出方向と凝固液の流れの方向とを一致させることが望ましいが、装置の設計上から一致させることができない場合には、吐出方向と凝固液の流れ方向とが90°以下の角度となるようにすればよい。また、凝固液の流速を混合コロイド分散液の吐出速度より速くして糸条を延伸させることにより、微細粒子複合化デンプン繊維の

mixture of namely, 1 wt% extent there are also some which mixing effect of the fine particle does not reveal, mixing trace amount of 0.1 weight% extent, there is also a fine particle which mixing effect reveals. In a word if above minimum effective amount which mixing effect of fine particle reveals it should have mixed. general mixing ratio of fine particle, fine particle is 30 weight % or more and 70 wt% or less vis-a-vis the total weight of starch and fine particle.

[0023] Swelling doing starch, after cooling once, maintaining in the specified temperature, yarn-spinning it does fine particle / starch mixed colloid dispersion which it acquires, but as for temperature of mixed colloid dispersion at time of yarn-spinning it is undesirable to maintain in 50 to 60 °C. When temperature of mixed colloid dispersion changes, because viscosity changes, when fine particle composite making starch fiber which is stabilized is not acquired, in addition the temperature decreases considerably, it is known that aging of starch is caused.

[0024] Next, inserting fine particle / starch mixed colloid dispersion which is maintained in the specified temperature, in sealed container, you apply constant pressure, quantity of option, from the nozzle orifice which had aperture and geometry you discharge in the coagulation bath, it can make fine particle composite making starch fiber with so-called wet spinning method. This kind of wet spinning method of to be method which common use is done from until recently as viscose fiber or other spinning method, therefore existing spinning equipment can be utilized. diameter (thickness) of fine particle composite making starch fiber can adjust aperture of nozzle by fact that it changes.

[0025] Ammonium sulfate, sodium sulfate, magnesium sulfate, ammonium phosphate and sodium carbonate, be able to use aqueous solution of salt which causes electrolyte at ammonium chloride or other under water as coagulation liquid in coagulation bath, ammonium sulfate especially is desirable. When concentration of coagulation liquid is low, coagulating effect is not acquired by the fully, brine solution of 30 to 40 wt% concentration is desirable generally.

[0026] Administering regular agitation to coagulation liquid in coagulation bath, it causes the flow of coagulation liquid. Direction of current and rate of coagulation liquid exert influence on fiber length and strength of fine particle composite making starch fiber which is acquired. To try to become flow of yarn which fine particle / starch mixed colloid dispersion which discharges in namely, coagulation liquid stabilizes, it is desirable to agree with discharge direction of mixed colloid dispersion and direction of current of the coagulation liquid, but when it is not possible, to agree in regard to design of equipment, flow direction of discharge

水に対する不溶化および強度を向上させることができる。しかし、凝固液の流速を過度に速くすると、糸条が凝固浴中でちぎれてしまい、所望繊維長の微細粒子複合化デンプン繊維が得られない場合もある。上記の理由から、凝固液の流れの方向や流速は、所望の微細粒子複合化デンプン繊維が得られるような条件を予備実験により定めておく必要がある。

【0027】この発明により得られる微細粒子複合化デンプン繊維の応用例としては、例えば二酸化チタンのごとき白色顔料を複合化したデンプン繊維は、デンプン繊維のみのもつ透明性を白色顔料で隠蔽できるため、これを紙に混抄することにより紙の不透明性を向上させることができる。さらに、導電性の微細粒子を複合化したデンプン繊維を用いて帯電防止紙を製造することも可能である。

【0028】

【実施例】以下に実施例を挙げてこの発明を更に説明する。

【0029】実施例1

カオリクレー（商品名「SFカオリン」、服部鉱業（株）製）5重量%と、混合比率を種々に変えた馬鈴薯デンプンとトウモロコシデンプンの混合物5重量%とから、固形分濃度10重量%の水混合懸濁液を調製し、これを95℃に加熱してデンプンを膨潤させて微細粒子/デンプン混合コロイド分散液とした。硫酸アンモニウムの40重量%水溶液中の凝固液からなる凝固浴中に口径0.3mmの丸型ノズルを設置し、上記の微細粒子/デンプン混合コロイド分散液を55℃の一定温度として吐出圧力2kg/cm²でノズルから凝固浴中に吐出させ、微細粒子複合化デンプン繊維を製造した。吐出に際しては、凝固浴を攪拌して微細粒子/デンプン混合コロイド分散液の吐出方向と凝固液の流れ方向が30°の角度になるようにした。

【0030】馬鈴薯デンプン（ポテト）とトウモロコシデンプン（コーン）との混合比率と得られた微細粒子複合化デンプン繊維の平均繊維長分布との関係を表1および図1に示す。

direction and coagulation liquid becomes angle of 90 deg or less that should have tried. In addition, making flow rate of coagulation liquid quicker than extrusion rate of the mixed colloid dispersion, insolubilization and strength for water of fine particle composite making starch fiber by the drawing doing yarn, it can improve. But, when flow rate of coagulation liquid is made quick excessively, yarn in coagulation bath, when tearing you put away, fine particle composite making starch fiber of desired fiber length is not acquired, it is. From above-mentioned reason, as for direction of current and flow rate of coagulation liquid, it is necessary to decide kind of condition where the desired fine particle composite making starch fiber is acquired with preparatory experiment.

[0027] As application example of fine particle composite making starch fiber which is acquired by this invention, as for the starch fiber which for example titanium dioxide or other white pigment composite making is done, transparency which only the starch fiber has hiding because it is possible with white pigment, opaqueness of paper it can improve this by blending doing in paper. Furthermore, also it is possible to produce antistatic paper making use of the starch fiber which fine particle of electroconductivity composite making is done.

[0028]

[Working Example(s)] Listing Working Example below, further more you explain this invention.

[0029] Working Example 1

From blend 5 weight % of kaolin clay (tradename "SF kaolin", Hattori mining Ltd. make) 5 weight % and potato starch and cornstarch which changed mixing ratio into various, manufacturing water mixed suspension of solid component concentration 10 weight %, heating this to 95 °C and swelling doing starch it made fine particle / starch mixed colloid dispersion. It installed round nozzle of aperture 0.3 mm in coagulation bath which consists of the coagulation liquid in 40 weight % aqueous solution of ammonium sulfate with extrusion force 2 kg/cm² from nozzle discharging in coagulation bath with above-mentioned fine particle / starch mixed colloid dispersion as the constant temperature of 55 °C, it produced fine particle composite making starch fiber. At time of discharge, agitating coagulation bath, discharge direction of the fine particle / starch mixed colloid dispersion and flow direction of coagulation liquid that tried become the angle of 30 degree.

[0030] Between potato starch (potato) and of cornstarch (corn) with relationship of mixing ratio and mean fiber length distribution of fine particle composite making starch fiber which is acquired is shown in the Table 1 and Figure 1.

[0031]

表 1 |

	デンプン混合比率 (重量%)	平均繊維長分布
	[ポテト/コーン]	(mm)
3	0/100	2.1 ± 0.2
4	30/70	5.9 ± 0.5
9	50/50	6.4 ± 0.4
5	70/30	8.9 ± 0.7
	100/0	10.5 ± 1.8

表 1 および図 1 からわかるように、曳糸性のある馬鈴薯デンプンの比率が増すことにより、平均繊維長が大きくなり、逆に曳糸性のないトウモロコシデンプンの比率が増すことにより、平均繊維長が小さい微細粒子複合化デンプン繊維が製造できる。

[0032] 実施例 2

馬鈴薯デンプンとトウモロコシデンプンの混合比率を 50 : 50 重量%と一定にしたデンプンと、カオリンクレー（同上）とを、これらの混合比率を種々に変えて固形分濃度 10 重量%の水混合懸濁液を調製し、その他は実施例 1 と同様にして微細粒子複合化デンプン繊維を製造した。

[0033] デンプン（馬鈴薯デンプンとトウモロコシデンプンの混合比率 50 : 50 重量%）とカオリンクレー（微細粒子）との混合比率と、得られた微細粒子複合化デンプン繊維の平均繊維長分布との関係を表 2 に示す。

[0034]

表 2 |

	デンプンと微細粒子の混合比率 (重量%)	平均繊維長分布
	[デンプン/微細粒子]	(mm)

[0031]

Table 1

	Starch mixing ratio (weight %)	mean fiber length distribution
	[Potato / cone]	(Mm)
	0/100	2.1 +/- 0.23
	30/70	5.9 +/- 0.54
	50/50	6.4 +/- 0.49
	70/30	8.9 +/- 0.75
	100/0	10.5 +/- 1.8

As understood from Table 1 and Figure 1, mean fiber length becomes large due to the fact that ratio of potato starch which has fiber pulling behavior increases, can produce fine particle composite making starch fiber where mean fiber length is small due to the fact that ratio of cornstarch which does not have fiber pulling behavior conversely increases.

[0032] Working Example 2

Mixing ratio of potato starch and cornstarch 50:50 weight% and starch and the kaolin clay (same as above) which are made fixed, changing these mixing ratio into various, it manufactured water mixed suspension of solid component concentration 10 weight%, other things it produced fine particle composite making starch fiber with as similar to Working Example 1.

[0033] Starch (mixing ratio 50:50 weight % of potato starch and cornstarch) with relationship between mixing ratio of kaolin clay (fine particle) and the mean fiber length distribution of fine particle composite making starch fiber which is acquired is shown in the Table 2.

[0034]

Table 2

	Mixing ratio (weight %)	mean fiber length distribution of starch and fine particle
	[Starch / fine particle]	(Mm)

10/90	0	10/90	0.5 +/- 0.04
5 ± 0.04			
30/70	4	30/70	4.2 +/- 0.56
2 ± 0.56			
50/50	6	50/50	6.4 +/- 0.49
4 ± 0.49			
70/30	7	70/30	7.6 +/- 0.33
6 ± 0.33			
90/10	10	90/10	10.7 +/- 1.54
7 ± 1.54			
100/0	11	100/0	11.6 +/- 1.83
6 ± 1.83			

表2からわかるように、微細粒子の混合比率は90重量%でも混合可能であり、このときに微細粒子複合化デンプン繊維を顕微鏡で観察したところ繊維状を有していた。

As understood from Table 2, mixing ratio of fine particle was blendable even with 90 weight %, when this time fine particle composite making starch fiber is observed with the microscope it had possessed fiber.

【0035】実施例3

酸化チタン（商品名「タイペークW-10」、石原産業（株）製）と、馬鈴薯デンプンとトウモロコシデンプンの混合比率を種々に変えたデンプンとを、種々の混合比率で混合し、固形分濃度10重量%の水混合懸濁液を調製し、その他は実施例1と同様にして微細粒子複合化デンプン繊維を製造した。

[0035] Working Example 3

Titanium dioxide (tradename "Tipaque W-10", Ishihara Sangyo K.K. (DB 69-428-8788) make) with, it mixed with potato starch and starch which changed the mixing ratio of cornstarch into various, with various mixing ratio, manufactured the water mixed suspension of solid component concentration 10 weight %, other things it produced the fine particle composite making starch fiber with as similar to Working Example 1.

【0036】酸化チタンと馬鈴薯デンプン（ポテト）とトウモロコシデンプン（コーン）との混合比率と、得られた微細粒子複合化デンプン繊維の平均繊維長分布との関係を表3に示す。

[0036] Relationship between mixing ratio of titanium dioxide and potato starch (potato) and the cornstarch (cone) and mean fiber length distribution of fine particle composite making starch fiber which is acquired is shown in Table 3.

【0037】

[0037]

表3 |

酸化チタン 繊維長分布	デンプン混合比率 (重量%)	平均繊維長分布
(重量%)	[ポテト/コーン]	
(mm)		
30	70 [30/70]	5.
5 ± 0.61		
50	50 [50/50]	5.
4 ± 0.45		
70	30 [70/30]	5.

Table 3

Titanium dioxide fiber length distribution	starch mixing ratio (weight %)	mean fiber length distribution
(Wt%)	[Potato / cone]	(Mm)
30	70 [30/70]	5.5 +/- 0.61
50	50 [50/50]	5.4 +/- 0.45
70	30 [70/30]	5.2 +/- 0.88

2 ± 0.88

表3からわかるように、微細粒子の混合比率が変わっても、曳糸性のあるデンプンと曳糸性のないデンプンとの混合比率を変化させることにより、ほぼ同じ平均繊維長分布をもたせることができる。

[0038]

【発明の効果】以上の説明からわかるようにこの発明によれば、下記のような効果が得られる。

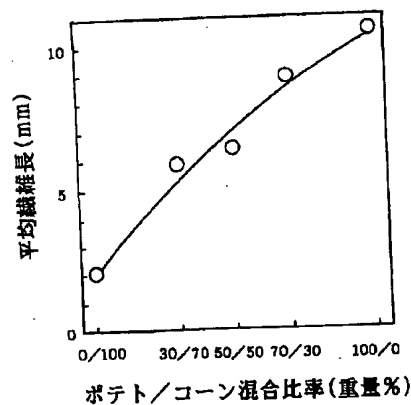
1) 曳糸性のあるデンプンと曳糸性のないデンプンとの混合比率を変えることにより、微細粒子複合化デンプン繊維の平均繊維長分布を任意の範囲で制御することができる。

2) 微細粒子の混合比率は、90重量%程度まで混合することができる。

3) 繊維長が制御された微細粒子複合化デンプン繊維が用途に応じて使い分けができるため、従来のデンプン繊維を使用したときには得られなかった効果の発現が期待でき、デンプン繊維の用途拡大を図ることができる。

【図面の簡単な説明】

【図1】デンプンと微細粒子（カオリンクレイ）の合計重量に対する微細粒子の混合比率を50重量%と一定にした場合の、馬鈴薯デンプン（ポテト）とトウモロコシデンプン（コーン）との混合比率と、得られた微細粒子複合化デンプン繊維の平均繊維長分布との関係を示すグラフである。



As understood from Table 3, mixing ratio of fine particle changing, it is possible almost to be able to give same mean fiber length distribution, the mixing ratio of starch which has fiber pulling behavior and starch which does not have fiber pulling behavior by changing.

[0038]

[Effects of the Invention] As understood from explanation above, according to this invention, as description below effect is acquired.

Mean fiber length distribution of fine particle composite making starch fiber can be controlled in range of the option 1) by changing mixing ratio of starch which has the fiber pulling behavior and starch which does not have fiber pulling behavior.

2) it can mix mixing ratio of fine particle, to 90 weight% extent.

3) fine particle composite making starch fiber where fiber length is controlled because it is impossible, to use properly according to application when using conventional starch fiber, be able to expect revelation of effect which cannot be acquired, it is possible to assure application enlargement of starch fiber.

[Brief Explanation of the Drawing(s)]

[Figure 1] Mixing ratio of fine particle for total weight of starch and fine particle (kaolin clay) the 50 weight % and it is, a potato starch (potato) when it makes fixed and a graph which shows the relationship between mixing ratio of corn starch (corn) and mean fiber length distribution of fine particle composite making starch fiber which is acquired.

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【図 1】

[Figure 1]